

Small-Angle Neutron Scattering Studies of Amorphous-Silicon-Based Solar Cell Materials

D.L. Williamson¹ and D.W.M. Marr²

¹Department of Physics, Colorado School of Mines, Golden, CO 80410

²Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401

ABSTRACT

The nanostructural heterogeneity of hydrogenated amorphous-silicon-based photovoltaic materials is being probed by small-angle scattering of neutrons. Films were deposited by two techniques, plasma-enhanced chemical vapor deposition (PECVD) and hot-wire chemical vapor deposition (HWCVD) using conditions that yield high quality films and devices. Comparisons of hydrogenated and deuterated films as well as effects of Ge alloying are highlighted.

1. Introduction

Extensive small-angle x-ray scattering (SAXS) studies of a-Si-based materials [1-3] have been supplemented more recently by the use of anomalous SAXS (ASAXS) [4,5] to yield new information on the non-uniformity of the Ge in a-SiGe:H alloy films. The addition of small-angle neutron scattering (SANS) measurements recently demonstrated no evidence for a light-induced change in the nanostructure [6], in contrast to an earlier report [7]. The possibility of substituting D for H allows additional information due to the large differences in scattering of neutrons by these two isotopes [8]. Although clear differences were seen in our first data, it was found that the D-containing gases induced significant changes during deposition of the PECVD material made under high H(D) dilution [6]. Here we examine more SANS comparisons of hydrogenated versus deuterated films and report first results from a-SiGe:H alloys.

2. Experimental

The SANS measurements were done at the NIST Center for Neutron Research on beamline NG-3 [9]. Data were collected over a momentum transfer range from $q = 0.05 \text{ nm}^{-1}$ to 3 nm^{-1} , using neutrons with wavelength 0.6 nm and two detector positions (2 m and 13 m from the sample). Several special samples were prepared for the SANS studies, some with deuterated gases, SiD_4 , GeD_4 , D_2 , used in place of SiH_4 , GeH_4 , and H_2 . Special, high purity FZ c-Si substrates were used with surface roughness below 0.5 nm in order to prevent extra background scattering. Multiple films of 1 to 2 μm thickness were prepared to allow stacking of up to 20 layers. IR spectroscopy was used to obtain bonded H and D contents in all of the samples and electron microprobe measurements provided the Ge fraction x in the $\text{a-Si}_{1-x}\text{Ge}_x\text{:H(D)}$ alloys.

3. Results and Discussion

Table I lists the compositions of the SANS samples discussed here. The NXX designation refers to HWCVD

samples made by NREL and the UXX designation to PECVD samples made by USSC.

Table I. H, D, and Ge compositions (of $\text{a-Si}_{1-x}\text{Ge}_x\text{:H(D)}$).

Sample #	Ge (x)	[H] at. %	[D] at. %
NH3	0	7	0
ND3	0	~ 1	4
NH5	0.15	3	0
NH6	0	8	0
UH3	0.40	13	0
UD3	0.56	< 0.5	7
UH4	0	14	0
UD4	0	11	8

We note that the pairs NH3/ND3, UH3/UD3, and UH4/UD4 were made under nominally identical conditions except for exchange of hydrogenated gases by deuterated gases. For the UH4/UD4 pair, only the diluting gas H_2 was replaced by D_2 , leading to the mixed [H,D] composition. A small amount of H was detected in ND3 in spite of the lack of any H-containing source gases. From the UH3/UD3 pair, it appears that more Ge has been incorporated with the deuterated gases.

Figure 1 shows the SANS data from the four NREL samples. The scattering signals span four orders of magnitude and there are significant differences in the shapes of the scattering curves. Note that the replacement of H by D has yielded a lower level of scattering at high q and this is consistent with the much reduced incoherent scattering by D versus H. In fact a value of $0.025 \text{ cm}^{-1}\text{str}^{-1}$ is predicted for 7 at. % H in NH3, in excellent agreement with the data at the highest q . If this q -independent contribution is subtracted from the NH3 data then the scattering curve is nearly identical to that from ND3. This suggests that the inhomogeneity in these samples is unrelated to the H(D) distributions, which is surprising in view of the NMR results from similar material [10]. The scattering from the a-SiGe:H alloy indicates a bimodal distribution of scattering objects, with the high and low q features corresponding to 4- and 32-nm-sized objects, respectively. This is consistent with the earlier SAXS results from alloys of similar x [11]. The scattering from NH6 is much stronger than from NH3 and of a shape corresponding to a higher density of smaller inhomogeneities. This would be consistent with the use of the ultra-high deposition rate of 12 nm/s, which has been shown by SAXS to yield a much higher void density [12].

Figure 2 shows the SANS data from the four USSC samples. Again, there are significant differences for the Ge alloys and the sample containing only D (UD3) shows a

much reduced incoherent scattering background. The values of the latter for the hydrogenated samples are in good agreement with prediction based on the [H] in Table I. Note for these pairs that the deuterated samples have significantly less scattering, indicating that non-uniform H(D) distributions are contributing to the signals or the D-containing gases have improved the nanostructure.

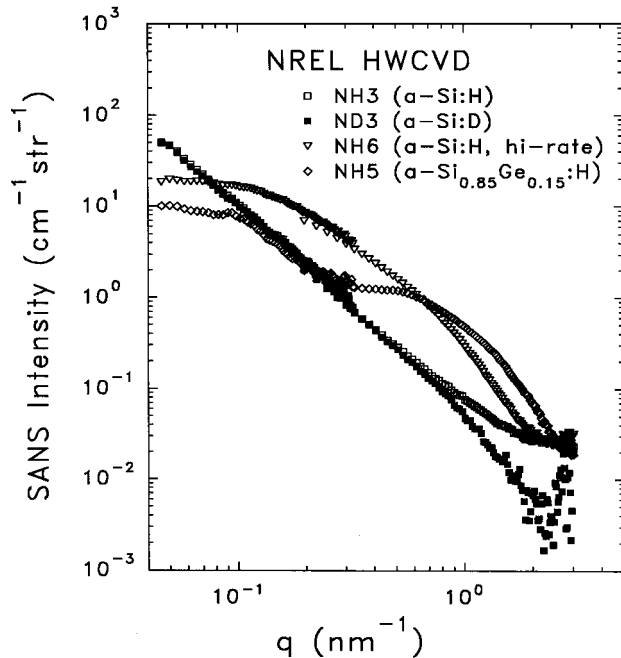


Fig. 1. SANS data from NREL films made by HWCVD.

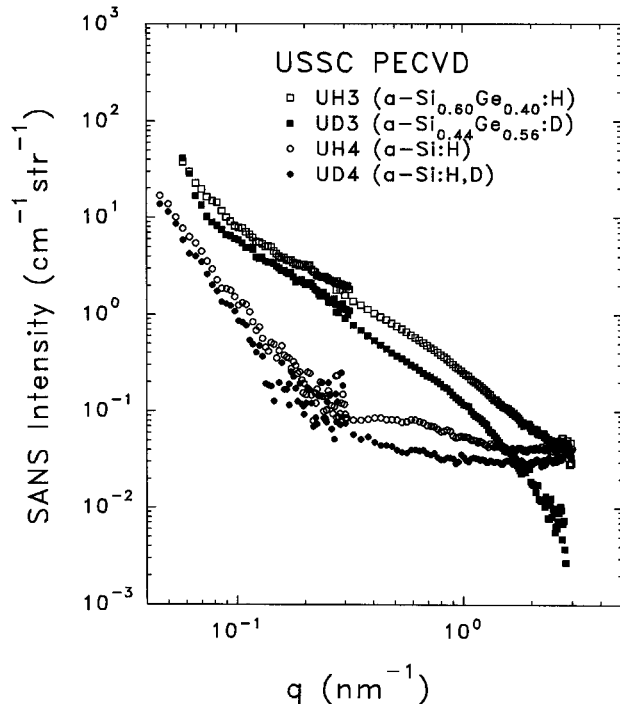


Fig. 2. SANS data from USSC films made by PECVD.

4. Conclusions

High quality SANS data have been obtained from PECVD and HWCVD films, including from a-SiGe:H alloys for the first time to our knowledge. Significant differences are found in the solar-grade materials from these two types of deposition methods.

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